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Preparation and room temperature ion irradiation of sputtered YBaCuO - films

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Abstract

YBaCuO-films (typical thickness 350 nm) were prepared by hollow-cathode dc-magnetron sputtering under optimized conditions onto yttria-stabilized ZrO_2 (YSZ) substrates (100-oriented). The as-prepared films were characterized by x-ray texture analysis and found to be epitaxially grown with c-axis orientation (mosaic spread < 0.3°). In addition, after lateral structuring by lithography and wet-chemical etching, the critical current densities were determined by transport measurements resulting in a maximum critical current density at 77 K of $4 \cdot 10^6$ A/cm^2 without an external magnetic field. By bombarding these bridges at 300 K with 200 keV He^+ ions, the superconducting transition temperature T_c, the resistivity ρ and the critical current density j_c could systematically be changed. In all cases, j_c reacted most sensitively to ion bombardment resulting in a strong decrease, which is in detail dependent on the film quality prior to irradiation.

1. Introduction

There have been many investigations on the new high-T_c-superconductors in the recent years especially to get detailed information on the microscopic correlation between defects and the mechanism of superconductivity.

To produce defects in a controlled way, ion irradiation is a often used tool. The kind of defects generated by particle bombardment strongly depends on the projectile and its energy. For example, by irradiation of YBaCuO-samples with heavy ions of energies in the upper MeV region, one can produce amorphous tracks, which act as additional pinning centers and enhance the critical current density in an external magnetic field [1]. For light particles with energies of a few 100 keV, it is expected that the created defects are predominantly point defects and small defect clusters, mainly in the sublattice of the oxygen atoms, which are easily displaced by ion bombardment [2]. Still in discussion is the amount of irradiation enhanced diffusion of oxygen out of the sample [3,4].

In order to provide additional information on these questions, we have investigated the effect of 200 keV He^+ irradiation on the superconducting transport properties of thin YBaCuO-films, thereby also paying attention to the influence of film quality on the effectiveness of the ion bombardment.

2. Film preparation

Thin films of YBaCuO with a typical thickness of 350 nm were prepared by sputtering with a hollow-cathode magnetron using a ring target of sintered stoichiometric $YBa_2Cu_3O_7$. Due to the special geometry of the sputtering gun, the bombardment of the growing film with negative ions emerging from the cathode surface is prevented, without a substantial decrease of the deposition rate (≃ 0.1 nm/s). Usually the gun is operated in the dc-mode with a current of 450 mA and a voltage of 130 V. The best films were obtained using a gas mixture of argon and oxygen with partial pressures of 0.5 mbar and 0.25 mbar, respectively. The films were deposited onto (100)-oriented yttria-stabilized ZrO_2 (YSZ) substrates, which were mounted onto a resistively heated stainless-steel holder. The temperature was controlled by a NiCr-Ni thermocouple.

The YBaCuO-films were prepared by an in situ two-step procedure [5]. The film deposition occured at substrate temperatures between 820 and 850 °C. In this way, the tetragonal YBaCuO-phase is obtained, which is slightly oxygen deficient. Then, in a second step, after reduction of the temperature to 420 °C, the films were heat-treated in a pure oxygen atmosphere of 1 bar. This step generates the transformation into the superconducting orthorhombic $Y_1Ba_2Cu_3O_7$ - phase. The preparation is finished by cooling down the films to room temperature within approximately 3 minutes.

The two basis preparation steps were performed in situ within two different UHV-chambers connected by a transfer system. This allows the use of metallic sputter targets, which are very sensitive to pure oxygen.

The transfer system additionally enables a periodic movement of the heated substrate holder during the deposition allowing the sputtering onto large area substrates. Preliminary results obtained for a YBaCuO-film, showed full superconductivity at 84 K over a length of 50 mm.

To clean the substrates before deposition or to pre-treat them in a controlled way, for example to create step edges, a broad beam RF ion gun is integrated into the preparation system.

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3. Film characterization

The as-prepared films could be characterized by x-ray diffraction on a 4-axis goniometer (Siemens D5000) in Bragg-Brentano geometry, where only lattice planes parallel to the substrate surface are detected.

Rocking curves (ω-scans) were measured with a stationary detector positioned at an appropriate diffraction angle 2θ by tilting the sample on the θ-circle through a suitable angular range. Such curves deliver the distribution of grains with a specific orientation (mosaicity) and their alignment with respect to the substrate surface normal.

Additionally by exploiting a special specimen holder, x-ray pole figures could be determined. In this methode, the detector is fixed at a certain diffraction angle 2θ, while the sample simultaneously is rotated latitudinally by an angle of χ (from 0° to 90°) and azimuthally by an angle of ϕ (from 0° to 360°) [6].

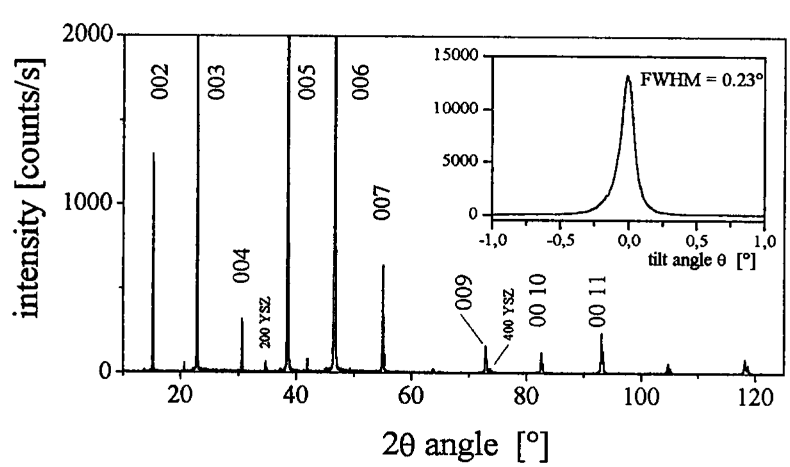
In the left part of figure 1 an x-ray diffraction pattern in Bragg-Brentano geometry of a YBaCuO-film prepared under optimized conditions onto a (100)-oriented ZrO_2 (YSZ) substrate can be seen. Only (00l)-lines are found indicating the highly textured growth of the film with the c-axis perpendicular to the substrate surface. Within the detection limit no foreign phases or a-axis orientations were found. The lattice constant c arises to 11.67 Å, which agrees well with the bulk value for $YBa_2Cu_3O_7$ [7]. The insert shows the rocking curve taken with the 2θ-angle fixed for the (005)-line. The measurement of the full width at half maximum (FWHM) yields a value of 0.23°, which clearly illustrates the rather good crystalline order in the film.

The right part of figure 1 exhibits a x-ray pole figure of the same specimen determined by the above mentioned method. Hereby the 2θ-angle is adjusted for the (113)-line. Four peaks are found, which are all located at the same latitudinal angle χ. The azimuthal angle ϕ of each line differs from the neighbouring by approximately 90°. This pattern clearly demonstrates the excellent c-axis oriented epitaxial growth and the strong alignment within the ab-plane. No evidence for any large angle tilt boundaries can be detected. Because a distinction between the a- and b-axis of the YBaCuO-system is beyond the solution of the diffractometer, a pronounced twinning structure of the film can not be excluded.

To quantify the superconducting transport properties of the sputtered YBaCuO - films a conventional four probe dc methode was applied.

Films prepared onto YSZ substrates under optimized conditions became superconducting with T_c's of 90 K and transition widths of less than 1 K. They had a resistivity ρ(100 K) of about 100 μΩcm, the residual resistivity ratio ρ(300 K)/ρ(100 K) amounts to about three (with a linear temperature dependence in between). In order to evaluate the critical current density the YBaCuO - films were patterned into striplines of typical 500 μm length and 20 μm width. For this purpose, a standard photolithography process was used, followed by wet-chemical etching with saturated H_3BO_3 and dilute H_3PO_4 [8]. For this procedure, no degradation of the film quality could be noticed. Electrical contacts were made by evaporating silver through a suitable mask, afterwards annealing in pure oxygen of 1 bar at 150 °C and then pressing thin indium wires onto the silver pads.

The critical current was defined as producing a voltage of 1 μV across the structured film.



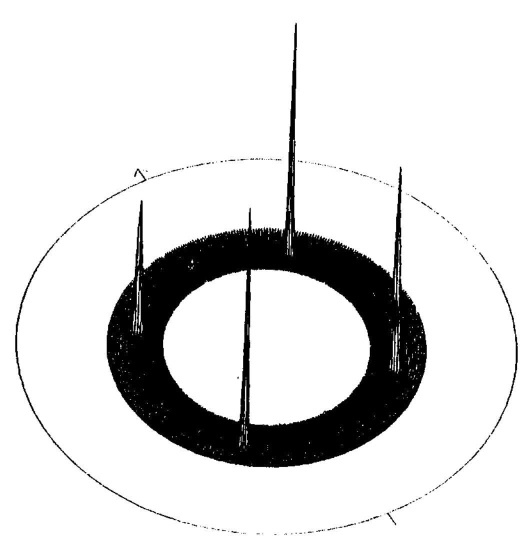


Figure 1. left part: x-ray spectrum in Bragg-Brentano geometry of a YBaCuO-film prepared under optimized conditions onto a (100) $Zr(Y)O_2$ substrate, the insert shows the rocking curve of the (005) line.
right part: pole figure of the same film, determined for the (113) line.

For the best films j_c values up to $4 \cdot 10^6$ A/cm^2 measured at T = 77 K without an external magnetic field were achieved. The temperature dependence of the critical current density was also determined and found to obey the relation $j_c \sim (1 - T/T_c)^{\alpha}$ with the value of α ranging between 1.2 and 1.5 .

4. Effect of Ion Irradiation

To study the influence of radiation induced disorder especially on the critical current density j_c, for all investigations patterned bridges of thin YBaCuO-films were used. The irradiations were performed with very low fluences up to a few 10^{13} cm^{-2} at room temperature with 200 keV He^+ ions at low beam currents (< 100 nA/cm^2) to avoid sample heating effects. The temperature of the sample holder was monitored simultaneously during bombardment and observed to increase not more than 1 K. The beam was directed parallel to the c-axis of the films and was scanned over the entire area to ensure homogenous damage. All experiments were carried out in situ in a vacuum of 10^{-6} mbar without taking the sample out of the chamber.

From a Monte Carlo simulation with Trim 87 [9] the mean range and straggling of 200 keV He^+ ions in $YBa_2Cu_3O_7$ can be estimated to be about 630 nm and 130 nm, respectively. Thus, the number of ions, which are implanted within the 350 nm thick films can be neglected. From the Trim calculation the number of displacements per atom (dpa) caused by the incident ions through nuclear collisions can also be deduced. Assuming an average threshold displacement energy of 20 eV, an ion fluence of $2 \cdot 10^{13}$ He^+/cm^2 corresponds to a damage level of $3 \cdot 10^{-4}$ dpa. Taking into account the particle density of $YBa_2Cu_3O_7$ one can additionally assess an average distance $\langle x \rangle_{def.}$ between defects created by irradiation, supposing that they are point defects, which are randomly distributed.

Figure 2 displays a series of resistivity versus temperature curves as a function of the irradiation fluence. The presented specimen was prepared under non-optimized conditions and therefore exhibited a slightly lower starting value of $j_c(77\text{ K}) = 7.5 \cdot 10^5$ A/cm^2. Proportional to the irradiation fluence a reduction of the transition temperature T_c and an increase of the resistivity ρ can be observed. Note that the shape of the transition curves $\rho(T)$ does not change significantly with fluence ϕ. Also nearly unaffected is the metallic behavior of $\rho(T)$, as indicated by the almost equal slope $d\rho/dT$ of the various curves. Consequently, the films obey the Matthiessen rule in the sense that the irradiation induced defects primarily act as additional scattering centers raising the residual resistivity.

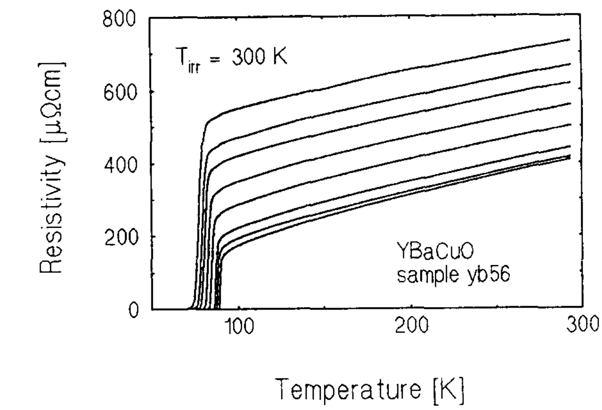


Figure 2. Resistivity versus temperature curves as a function of the irradiation fluence. For increasing resistivity, the fluences are: 0 , 0.3 , 0.6 , 1.0 , 1.5 , 2.0 , 3.0 , 4.0 • 10^{13} He^+/cm^2.

Both features of the resistivity versus temperature curves are indicative for the high quality and homogeneity of the samples.

The overall behavior of the transition curves $\rho(T)$ upon irradiation is found to be independent of the quality of the films as judged from the starting value of j_c. Nevertheless the effectiveness of the ion bombardment is strongly connected to these values. This is clearly demonstrated in figure 3, where the transition temperature T_c including the transition width δT_c (bars) and the resistivity $\rho(100\text{ K})$ are plotted as a function of ion fluence for two YBaCuO-films of different quality. This also could explain the relative low fluences as given in figure 2 in comparison to e.g. [3].

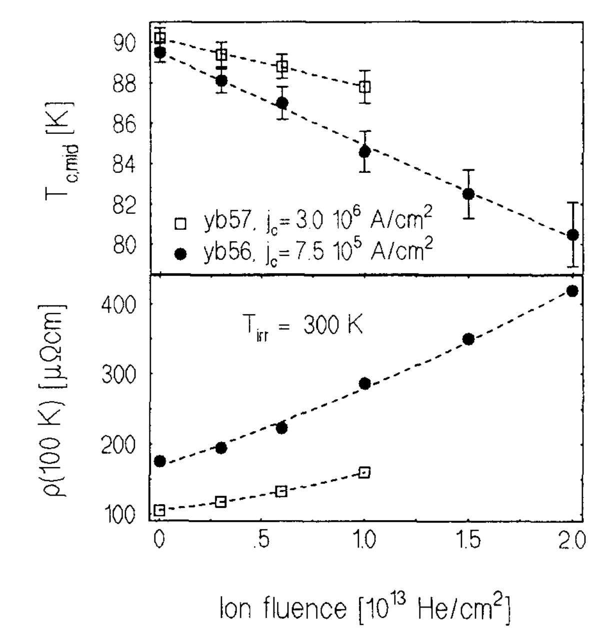


Figure 3. Transition temperature T_c including transition width δT_c (bars) and resistivity $\rho(100\text{ K})$ vs. ion fluence for two YBaCuO-films with different starting values of $j_c(77\text{ K})$.

Though for both films a linear decrease of T_c is observed, the corresponding slopes depend on the film quality prior to irradiation. On the other hand, in both cases the transition width is hardly affected by the bombardment proving again the homogeneous defect distribution. The resistivity ρ(100 K) shows an increase with fluence, which can be described as exponential. Within the above fluence range no saturation was observable. Both points confirm the results from [10].

The fact, that samples with lower starting values of j_c are stronger affected by ion irradiation than optimized films, has also been reported in [11].

The property found to be influenced most by ion irradiation, is the critical current density j_c. For example, after a fluence of $1.5 \cdot 10^{13}$ He^+/cm^2, j_c(77 K) is reduced by nearly four orders of magnitude, while $T_{c,down}$ still remains above 81 K. The reaction of j_c(77 K) upon particle bombardment is depicted in figure 4 for two YBaCuO-films of different quality, demonstrating that samples with a minor perfection are stronger affected by the ion irradiation. Plotting the critical current density versus the average distance $<x>_{def.}$ between defects, shown in the insert of figure 4, gives a clear drop of j_c(77 K) at values of $<x>_{def.}$, which are comparable to the superconducting coherence length ξ_{ab} in the $YBa_2Cu_3O_7$ - system. Such a relation for the critical current density was also reported for MeV He^+ ion irradiation [12].

It is also worth noting that we observed a tendency, that it makes a difference wether a certain ion fluence is applied in one "shot" or subdivided and applied in a stepwise manner providing some annealing time (typical 24 hours) between each subfluence.

Furthermore, a strong influence of the ion irradiation on the temperature dependence of j_c was discovered, pointing to the creation of weak links by particle bombardment. These results will be published elsewhere.

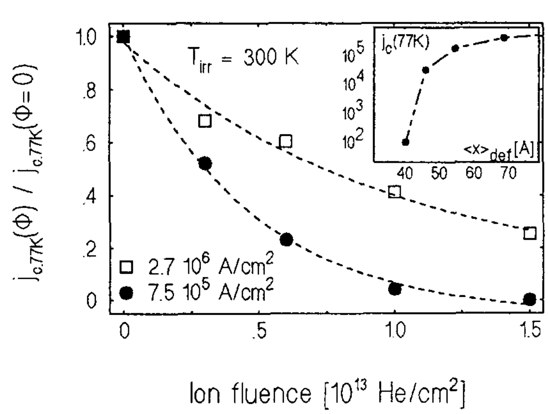


Figure 4. j_c(77 K) as a function of ion fluence for two YBaCuO-films of different quality. The insert shows a plot of j_c(77 K) versus the average distance $<x>_{def.}$ between defects.

5. Summary and conclusion

We have prepared thin films of YBaCuO on (100) ZrO_2 (YSZ) substrates by reactive sputtering using an hollow cathode magnetron. By x-ray texture analysis the films were found to be epitaxially grown with c-axis orientation (mosaic spread < 0.3°). Transport measurements on patterned bridges delivered critical current densities up to $4 \cdot 10^6$ A/cm^2 at 77 K without external magnetic field. Irradiation with 200 keV He^+ ions at room temperature leads to a degradation of the superconducting transport properties, among which the critical current density j_c reacts most sensitive. The irradiation induced changes depend strongly on the initial quality of the samples.

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